10/088990
JC13 Rec'd PCT/PTO 25 MAR 2002

Dr. Scheffler/MH
04.08.1999

"**Thin dirt-repelling coatings**"

This invention relates to compositions for preparing dirt-repelling functional coatings for stainless steel surfaces and to a process for coating stainless steel surfaces.

In the domestic, sanitary and clinical sectors and also in the food processing and pharmaceutical industries, a large number of the appliances, equipment and machines used are made of stainless steel. Due to its high resistance to corrosion, the surface of the stainless steel is polished or brushed and then used without further coatings. In this form, stainless steel is very susceptible to soiling by foodstuffs and cleansing agents or by fingerprints. A number of surface treatments have been suggested for improving the scratch-resistance of the surface and avoiding soiling. These have included both lacquer processes based on solvents or aqueous systems, as well as aqueous electrodepositable dipping lacquers or powder coatings. These coatings are intended to improve the soiling behavior and the scratch-resistance of the surface. However, using such coatings, the original appearance of the substrate is altered because they have very obvious gloss or color modifications when compared with untreated stainless steel.

JP-A-07/258599 (1995) describes paints based on an acrylic polyol resin, at least one binder based on isocyanate compounds or melamines, at least one sol of metal oxides and also catalysts and antioxidants. It is disclosed that these compositions are suitable for use as paints which are weather-resistant and have better surface hardness than traditional paints based on acrylate resins, and have good scratch-resistance and resistance to soiling. They are intended for lacquering wagons, building materials and also, inter alia, stainless steel.

JP-A-07/171496 (1995) describes coatings consisting of a polyester resin and a top coat of a silicate resin as well as the use thereof for coating stainless steel for outdoor applications.

JP-A-04150976 (1992) describes scratch-resistant and contamination-resistant coated stainless steel materials the surface coatings for which consist of a linear polyester resin and a melamine resin.

JP-A-01/151409 describes stainless steel surfaces having a surface roughness of 1 to 2.5 μm which have been coated with a polysiloxane, polyurethane or acrylic resin. It is stated that the stainless steel sheets coated in this way are suitable for the external cladding of railway carriages, lift doors and the like.

JP-A-02/228372 (1990) describes a weather-resistant and soiling-resistant high-gloss, hard powder coating based on an acrylate polyester and a blocked polyisocyanate, as well as pigments for the coating of stainless steel.

Despite the extensive prior art there is still a need for improved coating agents and a process for coating stainless steel surfaces. In particular, these coating systems should, if possible, be based on aqueous binder systems. Good antisoiling behavior and scratch-resistance of the coated surfaces should be provided; in addition the natural appearance, in particular of brushed stainless steel surfaces, should be retained. No details relating to the last-mentioned property may be found in the prior art. There is also the object of providing a thin, monolayered coating system which also has, over and above the criteria mentioned above, a high resistance to strongly alkaline and acid cleansers, such as are used for kitchen equipment or machines in the food processing industry. Furthermore, the binder should be applied using a conventional method of application.

The solution according to the present invention, is given in the claims. This consists substantially of providing an aqueous composition which contains at least one dispersed polyurethane prepolymer, wherein the isocyanate groups are preferably present in a blocked form, furthermore the binder contains one or more cross-linkable polymer dispersions or dissolved polymers and also optional wetting agents and dispersants and flow control agents and also optionally other auxiliary substances and additives.

The present invention also provides a process for coating stainless steel with scratch-resistant, dirt-repelling and hydrolysis-resistant coatings which comprises:

(a) if required, the surface of the stainless steel is cleaned and degreased;

(b) optionally, the surface is then rinsed;

(c) optionally, the surface is treated with an adhesion promoter;

(d) the coating composition is applied in an amount such that, after curing, a coating is

obtained having a weight per unit area of 0.1 to 10 g/m^2, preferably 0.5 to 5 g/m^2;

(e) optionally, volatile constituents, in particular water, are evaporated off;

and

(f) then the coating is cured at temperatures between 100 and 250°C peak metal temperature (PMT) for a period of between 0.5 seconds and 40 minutes.

In a preferred embodiment, the coating agent is applied to the surfaces of the workpiece or metal strip by flow coating/squeezing, spraying/squeezing, suitable wiper or roller application or also by brush application.

If the stainless steel is not intended to be coated directly in a coil-coating process, but shaped stainless steel parts are to be coated, then a spray system commonly used in lacquering technology, such as airless, air-assisted or electrostatically-supported spray processes, are preferably used.

The preferred uses of coated stainless steel according to the present invention are the production of machines, equipment and appliances for the domestic, sanitary and clinical sectors and also for the food processing or pharmaceutical industries.

An essential constituent of the binder system to be used according to the present invention is a preparation of a polyurethane prepolymer which substantially no longer contains free isocyanate groups. This polyurethane prepolymer is prepared in a known way from hydroxy-functional polyesters, hydroxy-functional acrylates or epoxides and aliphatic or cycloaliphatic polyisocyanates. The aliphatic or cycloaliphatic polyisocyanates used for this purpose are preferably selected from the group consisting of 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$), 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethyl cyclohexane (isophorone diisocyanate, IPDI), cyclohexane 1,4-diisocyanate, hydrogenated xylylene diisocyanate (H_6XDI), 1-methyl-2,4-diisocyanato-cyclohexane, m- or p-tetramethylxylene diisocyanate (m-TMXDI, p-TMXDI), dimeric fatty acid diisocyanates, tetramethoxybutane 1,4-diisocyanate, butane 1,4-diisocyanate, hexane 1,6-diisocyanate (HDI), 1,6-diisocyanato-2,2,4-trimethylhexane, 1,6-diisocyanato-2,4,4-trimethylhexane and dodecane 1,12-diisocyanate ($C_{12}DI$). Optionally, the corresponding trimeric biuret or isocyanurate products of the previously-mentioned diisocyanates may also be used.

Suitable polyols are polyesters having molecular weights between 400 and 10000, preferably between 400 and 5000, which may be prepared by the condensation of dicarboxylic or tricarboxylic acids such as adipic acid, sebacic acid, glutaric acid, azelaic acid, suberic acid, 3,3-dimethylglutaric acid, terephthalic acid, isophthalic acid, hexahydrophthalic acid or dimeric fatty acids, with low molecular weight diols, such as ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol, dimeric fatty alcohols, glycerol or trimethylolpropane. Another group of polyols suitable for use according to the present invention are polyesters based on ε-caproplactone, also termed "polycaprolactones". Hydroxy-functional polycarbonates may also be used as the polyol component in the polyurethane preparation for use according to the present invention. Polyesterpolyols of oleochemical origin, however, may also be used. These types of polyesterpolyols may be prepared, for example, by complete ring-opening of epoxided triglycerides of an at least partly olefinically unsaturated fatty acid-containing fatty mixture with one or more alcohols having 1 to 12 carbon atoms and subsequent partial transesterification of the trigyceride derivative to give alkylesterpolyols having 1 to 12 carbon atoms in the alkyl group. Other suitable polyols are polycarbonate-polyols and dimeric diols (Henkel) and castor oil and derivatives thereof. Polytetramethylene glycols which are prepared, for example, by the acid polymerisation of tetrahydrofuran may also be used, at least in admixture with other components, as polyols. In this case, the molecular weight of the polytetramethylene glycols is between 200 and 6000, preferably 400 to 4000.

Known hydroxy-functional acrylates or methacrylates may also be used as polyols; the molecular weight thereof is between about 400 and 10000.

Since the polyurethane preparations are aqueous systems, the polyurethane prepolymers generally have no free isocyanate groups but they are, at least to a large extent, blocked using blocking agents. These blocking agents are selected from aldoximes, ketoximes, lactams, imidazole compounds, β-dicarbonyl compounds, such as dialkyl malonates or ethyl acetoacetate. Further known blocking agents may be alcohols, phenols, in particular alkylphenols, thioalcohols, thiophenols, secondary amines, amides, imides or hydroxamates. The blocking groups are then released during curing or cross-linking of the binder system, optionally under the effects of a catalyst, so that the unblocked isocyanate groups may react with

other reactive groups, such as hydroxyl groups or amine groups, from other binder constituents and thus contribute to the increase in molecular weight and to cross-linking of the system.

Coating compositions to be used according to the present invention contain, as further cross-linkable polymer dispersions or polymer solutions, binders based on (meth)acrylate copolymers, hydroxy-functional polyurethane dispersions based on polyesterpolyols, polycarbonatepolyols or polyetherpolyols. Further binder components may be epoxide resin dispersions, optionally having free hydroxyl groups or modified with amines, or water-soluble or water-dispersible melamine/formaldehyde resins or urea/formaldehyde resins. Instead of (meth)acrylate homopolymer and/or copolymer dispersions, butadiene copolymer dispersions or styrene copolymer dispersions may also be used to at least some extent. The previously mentioned copolymers based on olefinically unsaturated monomers may still contain known cross-linkable comonomers. Acrylic acid, methacrylic acid, glycidyl (meth)acrylate, acrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N,N-bis-alkoxymethylmethacrylamide and similar thermally-cross-linkable groups may be mentioned by way of example, wherein the alkoxy groups may contain 1 to 4 carbon atoms. Furthermore, cross-linkers in the form of epoxide resin dispersions or known urea derivatives may also be used. (Meth)acrylate dispersions or emulsions, epoxide resins or methylolated melamine/formaldehyde resins, such as methoxymethyl-methylol-melamine, which cross-link either with themselves or with each other, are particularly preferred.

In addition to the previously-mentioned binders, the aqueous preparation according to the present invention also contains additives which have a positive effect on the flow properties and film-formation of the applied dispersions or solutions. Examples of these are small amounts of substantially volatile, organic, water-miscible solvents such as butyl glycol, 2-butanol, and solutions or dispersions of mercaptoesters, fluorinated polysilicone glycols, silicone glycols, low molecular weight acrylate copolymers, polyether/polysiloxane copolymers and similar flow control agents. Furthermore, so-called "cross-linkers" in the form of polyfunctional aziridine group-containing cross-linkers for carboxyl group-containing polymers or alternatively polyepoxide dispersions may be used. Furthermore, colloidal silica solutions may also be used as auxiliary agents. If the silica particles are present in nanoscale form, they increase the scratch-resistance of the coating without affecting the visual appearance thereof.

Preparations according to the present invention contain:

0 to 25 wt.%, preferably 5 - 10 wt.%, of polyurethane prepolymer (as active substance),

0.5 to 150 wt.%, preferably 1 to 100 wt.%, of cross-linking polymer components, based on the polyurethane active substance,

0.01 to 5 wt.%, preferably 0.1 to 1 wt.%, based on the total preparation, of flow control agent; and

2 to 15 wt.%, preferably 5 to 10 wt.%, based on the total composition, of film-forming solvents.

If the compositions do not contain a blocked polyisocyanate/polyurethane prepolymer, other cross-linking polymer components must be present, these being in particular epoxide resin emulsions combined with polyamine adducts (as a solution in water).

Here, the term "active substance" excludes the dispersion medium, such as water and volatile solvent, while these are included in the "total composition". The pH of the preparations is between 7.0 and 9.0.

It may be expedient, before applying the organic binder, to use an adhesion promoter. Examples of these types of adhesion promoters are Alodine NR 1453 (Henkel) and similar adhesion promoters based on hexaflurotitanates, phosphoric acid or polyphenols used in coil-coating processes, such as are disclosed in WO 99/16827 or WO 98/47631, for the pretreatment of metallic substrates. Furthermore, organophosphonic acids or organofunctional silanes may be used as adhesion promoters.

Apart from the previously-mentioned flow control agents and wetting agents and film-formers, pigments may be used only if their particle size thereof is within the nanometre range because preparations according to the present invention are intended to be transparent. Furthermore, conventional antioxidants and inorganic auxiliary agents may be used.

Coatings according to the present invention are very stable and have a high staining resistance with regard to a large number of agents, such as those which are common in the domestic sector and foodstuffs industry, for example black tea, black ink, condensed milk, fruit juices, vinegar, mustard, ketchup, mayonnaise and onion. The fingerprints which remain on the surface after handling uncoated stainless steel are also avoided with stainless steel which is coated according

to the present invention. They are also stable under the effects of acid and strongly alkaline cleansing agents, such as washing up liquids, oven cleaning sprays, so-called "steel gloss" or all-purpose cleansers even at temperatures of up to 60°C. The visual appearance of brushed surfaces is also retained in full, even though absolute degree of gloss measurements indicate differences from the uncoated stainless steel.

The present invention is intended to be explained in more detail by means of the following non-limiting Examples. Unless stated otherwise, all data relating to amounts in the following Examples are given as percentages, by weight, or parts by weight with respect to the total composition.

Examples

Coatings were prepared in the same way as described in JP-A-07/171496 and tested as to suitability as dirt-repelling functional coatings for stainless steel surfaces. The coatings exhibited severe yellow discoloration and were not resistant to acids and alkalis, such as those which occur in foodstuffs.

Also, coatings made from polyester resin and a melamine resin, analogous to those in JP-04/150976, produced thick yellowish layers and were not hydrolysis-resistant.

Coatings consisting of a polysiloxane and a polyurethane analogous to those in JP-A-01/151409 were not resistant to acids, alkalis or foodstuffs.

In the case of the following coatings in accordance with the present invention, brushed stainless steel sheets which had been pretreated with a 2.5 % strength solution of Ridoline C 72 (Henkel) for 20 to 30 seconds at 60°C in a spray process were used. Then, an adhesion promoter was applied using a lacquer coater or in a dipping bath and dried. The drying method for the adhesion promoter depended on the method of application: when using a lacquer coater, the coating was dried for 2 minutes at 70°C in an oven, and, when using the dipping method, the coated substrate was dried by blowing with compressed air after being dipped. Alternatively, 1 to 20 % strength solutions of Alodine NR 1453 or Granodine 1455 (both made by Henkel) were used as adhesion promoters. Then the dirt-repelling functional coatings according to the present

invention were applied with the aid of a lacquer coater or a laboratory spray gun so that a coating having a weight per unit area of 1 to 3 g/m^2 was produced after stoving at 170°C for 20 minutes in a circulating air oven. For coatings according to the present invention, binders and auxiliary agents were used as an aqueous dispersion or a solution in organic solvents so that the production of a homogeneous coating composition could be achieved by simply mixing and stirring. The individual results are listed in Tables 1 and 2 below.

Table 1 :

	Example	1	2	3	4	5	6	7	8
1	Fully deionised water	52.1	29.4	27.2	68.3	34.5	71.4	75	74
2	Butyl glycol	10.0	-	-	-	-	-	-	-
3	Dowanol DPM	-	10.0	10.0	-	-	-	-	-
4	Blocked polyisocyanate based on IPDI (28 wt.% in water)	35.7	53.6	53.5	-	35.7	-	-	-
5	Blocked polyisocyanate based on IPDI (45 wt.% in water)	-	-	-	-	-	22.2	-	-
6	PUR having temp. blocked isocyanate groups (40 wt.% in water)	-	-	-	-	-	-	25	-
7	PUR having blocked isocyanate groups (60 wt.% in water)	-	-	-	-	-	-	-	15
8	Acrylate copolymer emulsion (46 wt.% in water)	2.2	-	-	-	-	3.3	-	11
9	Polyurethane based on polycarbonate/diol (35 wt.% in water)	-	-	-	-	28.6	-	-	-
10	Epoxide resin emulsion (56 wt.% in water)	-	-	5.2	26.8	-	-	-	-
11	Aliphatic polyamine adduct (15 % soln. in water)	-	-	-	4.4	-	-	-	-
12	Fluoropolymer emulsion (50% perfluoro compd. in water)	-	-	-	-	1.0	-	-	-
13	Partly methylolated melamine resin (88 wt.% in water)	-	6.8	-	-	-	-	-	-
14	SiO_2 sol (12.5 wt.% in water)	-	-	-	-	-	3.1	-	-
15	Polyether-modified polysiloxane (52 wt.% in DPM)	-	0.2	-	-	0.2	-	-	-
16	pH	8.2	8.3	8.5	9.0	8.0	8.8	7.8	7.5

17	Gloss measurement 20° (gloss applied) Brushing long. (stand. 114) Brushing trans. (stand. 61)	58.8 30.9	68.8 46.1	83 44	80 48	84.3 49.7	52.2 29.3	75.2 42.9	21.4 16.5
18	Gloss measurement 60° (matt applied) Brushing long. (stand. 184) Brushing trans. (stand. 64)	63 35	82 64	–	–	–	–	–	–
19	Color measurement, yellowness b* value (standard 3.7)	4.4	4.0	3.2	3.6	4.3	4.4	4.8	3.9

In the preceding Table, DPM in row 3 means dipropylene glycol monomethyl ether. The blocked polyisocyanates in accordance with rows 4 and 5 are dispersed in water, cosolvent-free, polyisocyanate derivatives blocked with 2-butanoxime having a latent NCO content (calculated with respect to the solids) of 10 and 11%, respectively. The polyurethane resin (PUR) in accordance with rows 5 and 6 are anionic dispersions of polyurethane resins having cross-linkable, blocked isocyanate groups having a functionality greater than three. The acrylate copolymer emulsion in accordance with row 7 is a dispersion of (meth)acrylate copolymers consisting of C_1-C_4 esters of (meth)acrylic acid with N-alkylolacrylamide groups, viscosity 36 mPas/25°C, MFT 15°C. The polyurethane in accordance with row 9 is an anionic polyurethane dispersion based on an aliphatic polycarbonate which contains N-methylpyrrolidone as a film-forming auxiliary substance. The fluoropolymer emulsion in accordance with row 12 is a fluoroethylene/vinyl ether copolymer and is used, as is the polyether modified polysiloxane in accordance with row 15, as a surfactant to improve the substrate wetting behavior of the aqueous coating composition. The melamine resin in accordance with row 13 is a mixture of methoxymethylmethylolmelamine isomers.

The gloss was measured using a micro-TRI gloss measuring instrument from the Byck-Gardner Company. Since the surface of the stainless steel sheets resulted from a brushing procedure, the measurement was taken once in the same direction as that of the brushing procedure and once at right angles, and compared with a standard (a non-lacquered material). It may be seen that in both cases there is a significantly lower degree of gloss at right angles to the direction of brushing than in the direction of brushing. It may be seen from the

measured values that the optical impression of brushing after coating with the compositions according to the present invention is largely retained, and this was also confirmed in a visual assessment. The colorimetric determination of color intervals was determined using the CIELAB formula, wherein only the b-value was taken into account as an indication of the yellowing of the coating which was colorless in itself. As may be seen from the comparison with the uncoated standard in row 19, hardly any yellowing was detected in any of the coatings, and this was also confirmed in a visual assessment.

The results for the surface properties and the resistance tests for the coatings according to the present invention are summarised in Table 2 below. The surface properties, in this instance in particular the scratch-resistance and the sensitivity to showing fingerprints, are at least the same as the untreated standard for all the coatings according to the present invention and in most cases are much better than the untreated standard. The same applies to the resistance to common foodstuffs and mild cleansers. The compositions according to the present invention may even be designed in such a way that they are also resistant to very aggressive cleansers, such as oven cleaners or Ceran cleansers.

Table 2:

Ex.	Surface property			Resistance to					
	Finish (1)	Scratches (2)	Finger prints (3)	Food-stuffs (4)	Mild cleansers (4)	Aggress. cleansers (4)	Steam (5)	UV (6)	Temp. (7)
1	0	+	+	+	0	–	+	0	0
2	0	+	+	+	0	0	+	0	+
3	0	+	+	+	0	0	+	+	+
4	0	+	+	0	0	–	n.a.	n.a.	n.a.
5	0	+	+	+	0	–	n.a.	n.a.	n.a.
6	0	+	+	+	0	–	n.a.	n.a.	0
7	0	0	0	0	0	–	n.a.	n.a.	0
8	0	0	+	–	–	–	n.a.	n.a.	0

(1) optical assessment, no change in the desired appearance after resistance test

(2) determined with hard test rod 318, Erichsen Co.

(3) optical examination of fingerprints

(4) soiled test sheets are stored for 1 h at 60°C, washed with water and examined optically. Foodstuffs: mustard, tea, mayonnaise, ketchup, lemon juice, etc; mild cleansers: all purpose cleanser, washing up liquid etc,; aggressive cleanser: oven cleaner, Ceran cleaner, etc.

(5) 90° angled test sheets are treated with steam for 2 h and examined optically.

(6) Test sheets are placed in the Uvasol 2 irradiation system (Hönle) for 48 h. Then the ΔE value is determined using the "micro-color" color measuring instrument (Lange).

(7) Test sheets are subjected to a temperature of 150°C for 1 h. Then the ΔE value is determined using the "micro-color" color measuring instrument (Lange).

Test results

0	same as untreated standard
+	better than untreated standard
-	poorer than untreated standard
n.a.	not available